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Electron-Transfer Reactions at Metal-Solution Interfaces:

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ELECTRON-TRANSFER REACTIONS AT METAL-SOLUTION INTERFACES:
AN INTRODUCTION TO SOME CONTEMPORARY ISSUES

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ABSTRACT.   Some pivotal aspects of the contemporary treatment of
electrochemical kinetics for one-electron redox couples are outlined, and
some commonalities with homogeneous-phase electron transfers are pointed
out.   Two illustrative examples of the interplay between theory and
experiment are briefly discussed; specifically to the relation between
the rates of electrochemical and homogeneous-phase processes, and to the
recognition and elucidation of dynamical solvent effects.

I. INTRODUCTION

Examinations of the kinetics as well as thermodynamics of electron-
transfer reactions at metal electrodes have long been of concern not only
to electrochemists but also to others concerned with redox processes in
a variety of homogeneous as well as heterogeneous chemical environments.
This interest stems in part from the unique control of the electrical
variable afforded at metal-solution interfaces by the electrode
potential. In addition, such electrochemical processes involve inherently
only a *single* redox couple

$$Ox + ne^- \rightleftharpoons Red \qquad (1)$$

In contrast, electron-transfer reactions in homogeneous solution and at
most liquid-liquid interfaces involve *pairs* of redox couples.   The
thermodynamic and kinetic parameters that describe electrochemical
charge-transfer process therefore comprise fundamental characteristics
of such individual redox couples (so-called "half-reactions"), of value
to unraveling the behavior of redox processes on a more general basis.
While the characterization of electrochemical charge-transfer
reactions, often involving proton- and coupled atom-, as well as
electron-, transfers has a long and venerable history, understanding of
most kinetic and mechanistic aspects of electrode kinetics has tended to
lag behind that for analogous homogeneous-phase systems. This is
especially the case for the simplest type of reaction, involving
one-electron transfer between stable solution (Ox and Red) species.
Nevertheless, there are close parallels in the treatment of

heterogeneous- and homogeneous-phase processes of this type that allow a largely unified description to be developed.

Presented here is a brief overview of some fundamental features of electrode kinetics in relation to electron transfers in general. Discussion is also provided of two topics of research interest to the author, namely the relationship between the rates of heterogeneous- and homogeneous-phase processes, and the role of solvent dynamics in electron transfer. Rather than attempting a broadbased overview, then, the present account is written from an admittedly personal perspective. Nevertheless, the text is intended to illustrate some of the flavor of contemporary research in this area. A more comprehensive review of fundamental aspects, along with expanded citations, is to be found in ref. 1.

II. ELECTROCHEMICAL RATE PARAMETERS AND REACTION MECHANISMS

The basic characteristic of electrochemical reaction rates is their sensitivity to the applied electrode potential, E. In the absence of mass-transport limitations, the dependence of the current density for a redox process as in Eq. (1) upon E can be expressed as

$$i = i_o \{\exp[-\alpha nf(E-E_{eq})] - \exp[(1-\alpha)nf(E-E_{eq})]\} \qquad (2)$$

Here α is the cathodic transfer coefficient, $f = F/RT$, E_{eq} is the equilibrium potential for a solution containing given concentrations of Ox and Red, and i_o is the exchange current density. The last quantity denotes the equal (and counterbalancing) cathodic and anodic currents, i_c and i_a, respectively, that necessarily flow at $E = E_{eq}$, corresponding to the first and second exponential terms in Eq. (2). At least for electrode reactions displaying first-order kinetics, it is useful to define cathodic and anodic rate constants k_c and k_a, respectively. For one-electron first-order reactions, these are given by

$$k_c = i_c/FC_{ox}, \quad k_a = i_a/FC_{red} \qquad (3)$$

where C_{ox} and C_{red} are the bulk-phase (solution) concentrations of Ox and Red. From Eqs. (2) and (3),

$$k_c = k_{ex} \exp[-\alpha f(E-E^o)] \qquad (4)$$

The "standard" (or exchange) rate constant, k_{ex}, equals k_c (and k_a) measured at the standard electrode potential, E^o; note that $E^o = E_{eq}$ when $C_{ox} = C_{red}$. The standard potential, and hence k_{ex}, are of particular significance since E^o corresponds to the point where the interfacial potential experienced by the transferring electron equals the chemical-potential difference between Ox and Red, so that the electrochemical free-energy driving force for the overall electron-transfer reaction, ΔG^o_{rc}, equals zero.

Even for such ostensibly "single-step" electrochemical processes for solution-phase reactants, it is useful to separate the overall reaction into components associated with the formation of a "precursor

state" with the reactant in a suitable geometry within the interfacial region, and the "elementary electron-transfer step" where the activation energy barrier is surmounted with the reactant located within the precursor state [2]. This "preequilibrium" model differs from earlier treatments which presume (albeit vaguely) that the reaction proceeds via reactant "collisions" with the metal surface [2]. Provided that the formation of the precursor state involves a markedly smaller barrier than for electron transfer itself, we can decompose the overall observed rate constant, k_{ob} (cm s^{-1}), into a precursor equilibrium constant, K_p (cm), and a *unimolecular* rate constant, k_{et} (s^{-1}), characterizing the elementary electron-transfer step, according to [2]

$$k_{ob} = K_p k_{et} \tag{5}$$

In addition to its simplicity, this treatment has the virtue of enabling the influence of the interfacial environment upon the reactant thermodynamic stability to be separated from the vagaries of the electron-transfer step itself. Most importantly, the preequilibrium model is applicable to processes where the electrode-reactant interactions are weak and nonspecific as well as those where surface-reactant bonds are formed [2]. The former type includes most so-called "outer-sphere" processes, defined usually for electrochemical processes as those where the reactant is separated from the electrode surface by a layer of solvent or other molecules in the transition state. The latter reaction type can be considered to be "inner-sphere" processes, defined most generally as those featuring transition states where the reactant, or a coordinated ligand(s), binds to (or otherwise contacts) the metal surface [2]. For many (but by no means all) inner-sphere reactions, the electrode-reactant interactions are sufficiently favorable to enable the interfacial (precursor-state) reactant concentrations to be determined analytically, allowing K_p to be evaluated [3].

A similar situation can also be achieved in a few cases for outer-sphere electrochemical processes [4]. More commonly, however, diffuse-layer theory needs to be utilized to yield approximate K_p values for outer-sphere processes. In general, K_p can be related to the work of forming the precursor state from the bulk solution reactant, w_p, by [2]

$$K_p = K_o \exp(-w_p/RT) \tag{6}$$

where K_o (cm) is the "statistical" component of K_p. The latter can be approximated as the "reaction zone thickness", δr, denoting the effective range of precursor-state geometries (as separations from the metal surface) that contribute importantly to electron transfer; δr is typically of the order of 10^{-8} cm [5]. For reaction sites close to the outer Helmholtz plane (oHp), $w_p \approx ZF\phi_d$, where Z is the reactant charge number and ϕ_d is the diffuse-layer potential as deduced from the Gouy-Chapman model.

III. THEORETICAL RATE FORMULATIONS FOR THE ELECTRON-TRANSFER STEP

Of primary interest in electron-transfer kinetics is the understanding and rationalization of the observed rate constants, especially k_{et}, in terms of dynamical and energetic factors. The unimolecular rate constant can usefully be expressed in this fashion as [1,2,6]

$$k_{et} = \kappa_{el}\Gamma_n\nu_n \exp(-\Delta G^*/RT) \tag{7}$$

Here κ_{el} is the electronic transmission coefficient (≤ 1), Γ_n is the nuclear tunneling factor (≥ 1), ν_n is the nuclear frequency factor, and ΔG^* is the free energy of activation for the electron-transfer step. The first three terms together constitute the "preexponential factor" A_{et}, that describes the net dynamics of surmounting the classical free-energy barrier ΔG^*. It is important to recognize that this contemporary treatment of the preexponential factor, involving unimolecular activation within a preequilibriated precursor state, differs substantially from the classical (and flawed) description which emphasizes reactant-surface collisions as a prerequisite for electron transfer.

The ν_n term in Eq. (7) describes the net velocity along the reaction coordinate associated with the various motions which together constitute the nuclear reorganization barrier ΔG^*. The Γ_n term corrects the electron-transfer rate for the occurrence of sufficiently high-frequency motions so that significant nuclear-tunneling occurs *through* the classical free-energy barrier. In cases where the "inner-shell" barrier component, ΔG^*_{is}, arising from reactant bond distortions, is large, ν_n is often approximated by an appropriately weighted average of the relevant vibrational frequencies. In circumstances where the barrier is associated primarily with solvent reorganization, ΔG^*_{os}, the net dynamics of the solvent repolarization process can provide the predominant contribution to ν_n [7]. The role of solvent dynamics in electrochemical kinetics is considered in more detail below.

Complete control of the rate of electron-transfer barrier crossing by such nuclear dynamics will only be achieved when the electronic coupling between the donor and acceptor sites (the redox center and the electrode surface for electrochemical reactions) is sufficiently strong so to maintain so-called "reaction adiabaticity". Physically, this corresponds to the occurrence of sufficient resonance splitting between the lower and upper potential-energy surfaces in the vicinity of the intersection region (saddle point) so that the system stays primarily on the lower, reactive, surface. Such an "adiabatic" passage through the transition-state region corresponds to $\kappa_{el} \sim 1$ in Eq. (7). On the other hand, if the donor-acceptor electronic coupling is relatively weak, then a large fraction of passages through the intersection region will involve nonreactive transitions to the upper surface. For such "nonadiabatic" pathways, $\kappa_{el} \ll 1$, reflecting the relatively small fraction of reactive passages over the barrier.

It is important to recognize that for such nonadiabatic pathways, the net barrier-crossing frequency will be essentially *independent* of the nuclear dynamics, depending instead chiefly upon the degree of

electronic coupling. This point can be discerned readily by considering the following simplified, yet illustrative, Landau-Zener expression for the transmission coefficient κ_{el} [6]:

$$\kappa_{el} = 2[1 - \exp(-\nu_{el}/2\nu_n)]/[2 - \exp(-\nu_{el}/2\nu_n)] \tag{8}$$

The "electronic frequency factor" ν_{el} is given by

$$\nu_{el} = H_{12}^2(\pi^3/\Delta G^* h^2 k_B T)^{\frac{1}{2}} \tag{8a}$$

where h is Planck's constant, k_B is Boltzmann's constant, and H_{12} is the electronic coupling matrix element. While $\kappa_{el} \to 1$ for sufficiently strong electronic coupling (i.e. large H_{12}) so that $\nu_{el} \gg \nu_n$, Eq. (8) reduces to $\kappa_{el} \approx \nu_{el}/\nu_n$ for weaker coupling ($\kappa_{el} \ll 1$) so that $\nu_{el} \ll \nu_n$. Combining the preexponential factor A_{et} ($=\kappa_{el}\Gamma_n\nu_n$) from Eq. (7) with the latter nonadiabatic limit, yields $A_{et} = \nu_{el}\Gamma_n$, i.e., the net preexponential factor is proportional to H_{12}^2 [Eq. (8a)] yet *independent* of ν_n.

   While some small variations of A_{et} can also be anticipated, the dependence of k_{et} (and hence k_{ob}) upon the electrode potential arises primarily from variations in ΔG^*. Generally, for one-electron reactions we can separate ΔG^* into "intrinsic" and "thermodynamic" (driving-force) contributions [1]:

$$\Delta G^* = \Delta G_{int}^* + \alpha_{et}\Delta G_{et}^o \tag{9}$$

where α_{et} is the (cathodic) transfer coefficient (symmetry factor) for the electron-transfer step. The corresponding driving force, ΔG_{et}^o, can be related to the "standard overpotential" (E-E°) by [1]

$$\Delta G_{et}^o = F(E-E^o) + (w_s - w_p) \tag{10}$$

where w_s is the work of assembling the successor state (i.e., the state immediately following electron transfer) from the bulk-phase product. [Note that the combined term $(w_s - w_p)$ in Eq. (10) accounts for the difference in the potential dependence of the thermodynamics for the electron-transfer step and for the overall solution-phase reaction (1)].

   As already noted, it is convenient to separate the overall free-energy barrier into inner-shell (reactant distortional) and outer-shell (solvent reorganizational) components. For calculational purposes, it is convenient to apply this distinction to the intrinsic barrier, ΔG_{int}^*, yielding more manageable formulae. Thus the inner-shell component, ΔG_{is}^*, of ΔG_{int}^* can be estimated from the simple harmonic oscillator formula [6]:

$$\Delta G_{is}^* = 0.5 \sum f_i(\Delta a/2)^2 \tag{11}$$

where f_i is the force constant of each bond undergoing distortion by Δa as a result of electron transfer.

   The outer-shell component, ΔG_{os}^*, is usually estimated by means of the well-known formulae derived from dielectric-continuum theory, which for one-electron electrochemical reactions can be expressed as [8]

$$\Delta G^*_{os,e} = (e^2/8)(a^{-1} - R_e^{-1})(\epsilon_{op}^{-1} - \epsilon_s^{-1}) \qquad (12)$$

where a is the radius of the (presumed spherical) reactant, R_e is twice the reactant–metal surface distance (i.e., the reactant–image distance) in the transition state, and ϵ_{op} and ϵ_s are the so-called optical and static (zero–frequency) solvent dielectric constants, respectively. A related treatment for one–electron transfer between identical pairs of redox couples in homogeneous solution yields [8]

$$\Delta G^*_{os,h} = (e^2/4)(a^{-1} - R_h^{-1})(\epsilon_p^{-1} - \epsilon_s^{-1}) \qquad (13)$$

where R_h is the internuclear distance between the reactants (having equal radius a).

The extent to which these dielectric–continuum formulae provide reliable estimates of the solvent reorganization energy has engendered considerable discussion over the years [9]. A number of analytic treatments appearing recently provide somewhat modified descriptions of $\Delta G^*_{os,e}$ and/or $\Delta G^*_{os,h}$, most straightforwardly for the limit where R_e, $R_h \to \infty$, i.e., activation for "isolated" spherical reactants. In this limit, several improved treatments, such as that employing the "mean spherical approximation" (MSA) [10] and "nonlocal electrostatic" models [11], yield ΔG^*_{os} values that are significantly (ca 10–30%) smaller than in the dielectric continuum limit [12]. Moreover, a modified treatment of imaging effects suggests that the R_e^{-1} term in Eq. (12) is inappropriate in most circumstances [13]. Unfortunately, *direct* experimental tests of these models at metal–solution interfaces are absent; rate measurements by themselves provide only indirect comparisons since estimation of the preexponential component is not straightforward (vide infra) [13b]. Nevertheless, the applicability of the dielectric continuum approach for homogeneous–phase electron transfer can be tested more directly from the energies, E_{op}, of optical electron transfer within binuclear complexes, since E_{op} can be related simply to activation free energies for thermal electron transfer [14]. While the dielectric–continuum treatment has proved to be semiquantitatively reliable on this basis, somewhat improved agreement with experiment can be achieved by using more sophisticated models [12].

IV. INTERPLAY BETWEEN THEORY AND EXPERIMENT – GENERAL

At least for one–electron processes, there is much scope for utilizing such theoretical treatments to explore the rich diversity of experimental kinetics both at electrode surfaces and in solution. Indeed, a major application of kinetic theory in this vein is to collate, with an eye to rationalizing, sequences of rate parameters involving systematic variations in the system physical or chemical state [1]. Common examples of such experimental variables include electrode potential, temperature, electrode material, solvent composition, or reactant structure. Specific theoretical relationships, or formalisms, can be derived for this purpose, to confront with corresponding experimental data. Such tactics can be viewed as utilizing "relative"

theory–experiment comparisons [1].

An ultimate objective of chemical kinetic theory, however, is to predict rates of *individual* reactions in a given reaction environment. Such "absolute" theory–experiment comparisons can provide a demanding test of the underlying theoretical models. Their application, however, has been relatively limited in practice, even for outer–sphere one–electron processes, by the extensive structural and redox thermodynamic data that are required [15]. "Relative" theory–experiment comparisons are often less likely to exhibit deviations from expectations, due to the cancellation of terms in the theoretical expressions when the kinetics of closely related processes, and/or for a given process in different reaction environments, are compared. On the other hand, examination of relative rate parameters for judiciously chosen variations of physical and/or chemical state can yield much insight into *particular* factors that influence experimental systems since unwanted (and often unknown) components of the observed reactivities can thereby be held constant [1].

Outlined briefly below are two illustrative examples of such "relative" theory–experiment comparisons, specifically involving the rates of related electrochemical and homogeneous–phase reactions, and solvent effects upon the reaction dynamics. Emphasis is restricted here to a summary of the underlying concepts; numerical and other details can be found in the cited literature.

V. REACTIVITIES OF RELATED ELECTROCHEMICAL AND HOMOGENEOUS–PHASE PROCESSES

An issue of longstanding interest in electrochemical reactions concerns the relationship of the observed kinetics with those for the same redox couples involved in homogeneous–phase electron transfers. Given that the latter processes involve inevitably *pairs* of redox couples, several different types of comparisons can be envisaged. The simplest involve homogeneous self–exchange processes, since these reactions feature identical redox couple partners, thereby yielding the same reactants and products, so that $\Delta G^{o}_{et} = 0$.

The most common relationship used to examine the rates of outer–sphere electrochemical exchange, k^{e}_{ex} [Eq. (4)], and homogeneous self–exchange, k^{h}_{ex}, for a given redox couple is [16]

$$k^{e}_{ex}/A^{e} = (k^{h}_{ex}/A^{h})^{\frac{1}{2}} \qquad (14)$$

where A^{e} and A^{h} are the preexponential factors for the overall electrochemical and homogeneous–phase reactions, respectively (equal to $A_{et}K_{o}$) [1]. Equation (14) is derived for the special case where $R_{e} = R_{h}$ [Eqs. (12), (13)], predicted when the reaction partners (or the reactant–electrode pair) are in contact, so that $\Delta G^{*}_{os,e} = 0.5\Delta G^{*}_{os,h}$. The rate constants need to be corrected for electrostatic work terms, so that they reflect the kinetics of the elementary electron–transfer step [other than the inclusion of the statistical term K_{o}, Eq. (6)]. A related, yet distinct, formula results from the assumption that reactant–electrode imaging, and the inner–shell component of ΔG^{*}_{int}, can both be neglected, whereupon simply [17]

$$k_{ex}^{\bullet}/A^{\bullet} - k_{ex}^{h}/A^{h} \qquad (15)$$

In appropriate circumstances, both Eqs. (14) and (15) can provide acceptable fits tc experimental data [1].

Nonetheless, it is desirable to provide formalisms that are applicable in the more commonly encountered cases that involve homogeneous-phase cross reactions. A formulation designed for this purpose, which we have discussed recently [18], involves comparisons between a given electrochemical reaction and a corresponding homogeneous-phase reduction (or oxidation) that utilizes a reversible redox reagent Ox_2/Red_2, having a standard potential E_2^o. This treatment emphasizes the nature of metal surfaces as a special type of coreactant, having infinite radius and zero inner-shell barrier, yet a continuously variable "redox potential" equal to the applied electrode potential. Provided that the inner-shell barrier associated with Ox_2/Red_2 is small (or can be corrected for), and reactant-electrode imaging is unimportant, then the (work-term corrected) electrochemical rate constant measured at E_2^o, $k_2^{\bullet}$, is predicted on this basis to be related to the corresponding homogeneous-phase rate constant involving Ox_2/Red_2, k_2^h, by [18]

$$k_2^{\bullet}/A^{\bullet} - k_2^h/A^h \qquad (16)$$

Note that the form of Eqs. (15) and (16) are similar; indeed, the former is a special case of the latter. In the particular case where both the electrochemical and homogeneous-phase reactions are adiabatic ($\kappa_{el} \approx 1$) or at least feature comparable transmission coefficients, then[18] $A^h/A^{\bullet} - 4\pi N r_h^2$, where r_h is the reactant internuclear distance for the homogeneous-phase process, and N is Avogadro's number. Equation (16) therefore becomes

$$4\pi N r_h^2 k_2^{\bullet} - k_2^h \qquad (17)$$

The $4\pi N r_h^2$ term in Eq. (17) accounts for the difference between the planar and spherical reactant geometries characteristic of the electrode and homogeneous-phase coreactants, respectively, thereby converting the usual heterogeneous ($cm\ s^{-1}$) rate units into those ($M^{-1}s^{-1}$) appropriate for second-order solution-phase processes.

Given the various assumptions involved in deriving Eq. (17), widespread agreement with experiment is not anticipated. The virtues of this and related expressions lie instead in their treatment of related electrochemical and homogeneous-phase processes in an equivalent, if rather idealized, fashion. The manner and extent of the observed deviations of experimental rate data from Eq. (17) provide a useful measure of the degree to which additional, especially "specific" factors, such as electron tunneling, solvation dynamics, imaging interactions, etc., affect the kinetics of a given redox couple differently in the chosen heterogeneous- and homogeneous-phase reaction environments. Since the formal potential of only the homogeneous coreactant is required for the analysis, it is applicable to chemically irreversible and even multielectron electrochemical reactions.

In an exploratory comparison with experimental data [18], a number of outer-sphere electrochemical reactions at mercury-aqueous interfaces, including the reduction of various metal complexes and dioxygen, were found to exhibit rates that are significantly (up to ca 10^4 fold) greater than anticipated from homogeneous-phase data on the basis of Eq. (17). These differences were ascribed primarily to the occurrence of larger transmission coefficients in the electrochemical reaction environment. However, other factors, such as the occurrence of lower electrochemical free-energy barriers from metal imaging or other factors, may contribute to the observed behavior. Closer correspondence to the predictions of Eq. (17) are obtained, however, for some processes in nonaqueous media [18].

VI. DYNAMICAL SOLVENT EFFECTS IN ELECTROCHEMICAL KINETICS

Examining the kinetic as well as thermodynamic consequences of altering the solvent medium is of obvious fundamental interest in redox chemistry given the central role of solvation in all types of liquid-phase electron-transfer processes. The latter free-energy component (ΔG°_{et}) often provides the predominant contribution to the observed rate-solvent dependencies. However, this term can be held fixed by examining the solvent dependence of the *standard* rate constant, k_{ex}, (i.e., at E° in *each solvent*) thereby altering the electrode potential and therefore the free energy of the transferring electron(s), so to cancel the inevitable alterations in the solvation energies of Ox versus Red. Aside from solvent-dependent work terms, the remaining anticipated solvent effects upon k_{ex} arise at least from variations in the outer-shell reorganization energy, ΔG^*_{os}, and possibly also in the nuclear frequency factor, ν_n [Eq. (7)]. The presence of the former component has long been recognized, especially from the work of Marcus in the USA, Hush in England, and from Levich and Doganadze in the Soviet Union, dating back to the 1950's.

Perhaps surprisingly, the realization that electron-transfer rates can be influenced additionally by the *dynamics* of solvent reorganization, affecting ν_n as noted above, is of much more recent origin. This recognition arose from, and indeed forms an integral part of, the remarkable upsurge of interest in dynamical solvent effects in condensed-phase chemical processes in general that has occurred during the last decade [19]. We now outline in general terms the physical origins and likely consequences of such solvent dynamical effects in electrochemical kinetics. (See ref. 7 for further details and more complete literature citations).

In broad outline, the physical origin of such effects in electron transfer can be understood simply from the need to reorient collectively solvent dipoles in the vicinity of a redox center in order to achieve an appropriate nonequilibrium configuration so that electron transfer can occur. Even for simple dipolar fluids, however, it is important to distinguish between two distinct solvent dynamical regimes. In so-called low-dielectric friction media (associated loosely with low fluid viscosities), the rate of the necessarily *collective* dipolar motion will be limited only by the moment of inertia of the individual dipoles

together with the dielectric properties of the surrounding medium
[20,21]. Reaction dynamics controlled by solvent motion under these
"under impea" circumstances correspond to the so-called transition-state
theory (TST) limit, where the system passes smoothly along the reaction
coordinate from reactants to products. More commonly, however, it is
expected that the frequency of collective dipole motion will fall
significantly, or substantially below the TST value, ω_0, by irreversible
energy transfer from a given rotating dipole to its surroundings. This
latter occurrence, known as solvent "dielectric frictinn", corresponds
to slower "overdamped" (often-termed "diffusive") motion along the
reaction coordinate.

A key feature of such phenomena is that while the underdamped (TST)
dynamics are only mildly dependent on the solvent structure [21], the
overdamped frequencies are markedly solvent-sensitive. At least for
Debye solvents in the dielectric-continuum limit, the relevant overdamped
dynamics are described by the longitudinal solvent relaxation time, τ_L
[7,19,20]. This quantity is usually extracted from the "Debye"
relaxation time, τ_D, obtained from solvent dielectric-loss spectra, by
using [19]

$$\tau_L - (\epsilon_\infty/\epsilon_s)\tau_D \qquad (18)$$

where ϵ_∞ is the so-called "infinite-"(microwave) frequency dielectric
constant. [The observation of a single dielectric dispersion (τ_D) in the
dielectric loss spectrum is often referred to as "Debye-like" behavior.]
Interestingly, τ_L varies by at least 50 fold in common polar solvents at
ambient temperatures, from ca 0.2 to 10ps [22,23]. Measurements of
longitudinal relaxation dynamics can be made in some cases more directly
from time-dependent fluorescence Stokes shifts (TDFS) following ultrafast
laser-induced creation of charge-transfer excited states within suitable
chromophore solutes [24]. The time resolution of most published
measurements of this type is strictly inadequate for a reliable
description of the solvent dynamics relevant to electron-transfer
kinetics. However, recent subpicosecond TDFS measurements by Barbara and
coworkers have enabled solvation relaxation times, τ_s, to be extracted
even in low-friction media [24a,b]. In most cases, $\tau_s - (1.5-2)\tau_L$ [24b],
although relaxation components substantially shorter than τ_L are also
often observed (vide infra).

Of central interest are the relationships between the various
dielectric relaxation parameters and the resultant adiabatic barrier-
crossing frequency, ν_n, in Eq. (7). We consider first the situation
where the reaction coordinate is dominated by solvent, rather than
additionally by inner-shell, reorganization. In this case, in the TST
limit simply $\nu_n - \omega_0/2\pi$ [7,19]. The situation in the presence of
dielectric friction is somewhat more complicated, since the reaction
dynamic depend on the shape of the barrier top. For cusp-like barriers
(i.e., for small resonance splitting, H_{12}, of the barrier top), $\nu_n - \tau_L^{-1}$
[7,20]. As the barrier top becomes more "rounded" (i.e., H_{12} increases)
ν_n is predicted to diminish somewhat. A simple rationalization of the
latter is that barrier recrossings, yielding a lower net frequency of
successful diffusive passages through the intersection region and hence

a smaller ν_n, should become more prevalent as the barrier top becomes broader. For the degree of barrier-top roundedness required typically to yield adiabatic reaction pathways, ν_n is anticipated to be ca 2-5 fold smaller than τ_L^{-1} [25b]. One might therefore expect that at least approximate correlations between τ_L^{-1} and ν_n would often be obtained.

At least two further factors, however, are anticipated on theoretical grounds to complicate the nature of solvent dynamical effects on electron transfer. Firstly, as noted above, solvent relaxation components substantially faster than τ_L have been observed, even in "simple" dipolar fluids, from TDFS measurements. Additional faster relaxation times can also be extracted in some cases from dielectric loss spectra, such as in primary alcohols [25]. (Solvents exhibiting the latter behavior are referred to as "non-Debye" media.) Such higher-frequency components are predicted to exert disproportionately large contributions to the barrier-crossing frequencies, so that ν_n values substantially higher than τ_L^{-1} are often anticipated under these conditions [25].

Secondly, some deviations of the effective net relaxation time from τ_L are generally expected, even in Debye media, as a result of "solvent molecularity" effects, whereby solvent molecules in the immediate vicinity of the reacting solute behave differently from those in the "bulk" liquid [7,20]. An additional source of divergence from the simple expectation that $\nu_n - \tau_L^{-1}$ is expected for systems where the reaction coordinate contains substantial contributions from inner-shell (i.e., reactant vibrational) distortions as well as solvent reorganization. This situation has been discussed in detail by Marcus and coworkers [26]. Their treatment predicts that the dependence of ν_n upon solvent dynamics becomes increasingly muted as the frequency of inner-shell motion and/or the ratio $\Delta G_{is}^*/\Delta G_{os}^*$ increases; however, a substantial contribution from solvent dynamics can remain in the overdamped case even when $\Delta G_{is}^* - \Delta G_{os}^*$.

In the last five years or so, a sizable number of experimental studies have been published that aim to test the manner and extent to which such solvent dynamical factors influence activated electron-transfer reactions, both at electrode surfaces and in homogeneous solution [7]. The primary tactic employed has been to explore the solvent dependence of the rate constants, k_{ex}, for electrochemical exchange or homogeneous self-exchange of suitable one-electron redox couples that are anticipated or known to follow outer-sphere pathways. It is appropriate here to comment briefly on some of the limitations of, as well as key results from, these experimental studies, especially since insufficiently critical analyses have appeared on occasion in the recent literature. A more detailed discussion of these and related issues will be available elsewhere [27].

A key element in all these studies is the attempted separation of the observed k_{ex}-solvent dependencies into energetic and dynamical components, associated with variations in ΔG^* and ν_n, respectively. The reliable partition of these factors is often problematical, especially for electrochemical reactions, since the solvent-induced variations in ΔG^* typically have been estimated by using a theoretical formula, usually from Eqs. (12) or (13), rather than having a firm experimental basis. Admittedly, the *functional form* of Eq. (13) is typically roughly in

accord with some experimental E_{op} data for photoinduced electron transfers (vide supra) [14]. However, the uncertainties in the values of the "geometric factors" ($a^{-1} - R^{-1}$) which act to scale the resulting ΔG^* values, as well as in the details of the underlying model itself, can lead to substantial mistrust of the resulting estimated ΔG^*-solvent variations. This difficulty is heightened by the common expectation that the influence of the energetic and dynamical components upon the observed k_{ex}-solvent dependencies are often expected to be roughly comparable [22,23].

Fortunately, however, at least the *qualitative recognition* of the presence of solvent dynamical effects on this basis is aided by the roughly linear correlation between ΔG^*_{os} and log τ_L^{-1} (and hence log ν_n) expected for a number of solvents [22]. [This correlation is not unexpected since the outer-shell barrier ΔG^*_{os} in Eqs. (12) and (13) is determined primarily by the inverse optical dielectric constant ϵ_{op}^{-1}, and longer τ_L values are commonly associated with larger, more polarizable, solvents that also tend to exhibit greater ϵ_{op} values.] In a series of solvents with progressively decreasing ϵ_{op} values, then, in the absence of solvent dynamical effects the k_{ex} values will tend to decrease since the $\exp(-\Delta G^*/RT)$ term in Eq. (7) will diminish in this sequence. In the presence of solvent dynamical effects upon ν_n, however, this trend will be offset systematically since log ν_n tends to increase under these conditions. In some cases, the latter dynamical effect appears to dominate since net *increases* in k_{ex} are often observed in a given solvent sequence as τ_L^{-1} (and ϵ_{op}^{-1}) increase [22,23]. In this circumstance, strong evidence for the qualitative presence of solvent dynamical effects upon k_{ex} is at hand even in the *absence* of reliable corrections for the solvent-dependent barrier since the latter effect acts in the opposite direction [22].

Additional difficulties that can (and sometimes have) plagued the interpretation of solvent-dependent electrochemical kinetics in this vein include uncertainties in the work terms ("double-layer" effects) as the solvent is varied, and the erroneous neglect of (or inadequate correction for) solution resistance and related artifacts during the experimental evaluation of k_{ex}. The latter problem is particularly insidious since many reactions otherwise suitable for such studies are sufficiently rapid so to make corrections for solution resistance fraught with difficulty. Moreover, the effect of residual uncompensated resistance is often to depress the apparent k_{ex} values in a solvent-dependent manner that unfortunately mimics closely the anticipated influence of overdamped solvent dynamics. Unfortunately, then, the latter artifactual effect can easily be mistakenly identified as signaling a dominant role of solvent dynamics in electrochemical kinetics. For these and other reasons, multiparametric dielectric-continuum analyses of solvent effects in electrochemical kinetics, espoused by some authors [28], should be used only with extreme caution as an indicator of dynamical factors.

In spite of these pitfalls, the reliable quantitative diagnosis of dynamical solvent effects has been achieved in several systems. In our laboratory, we have preferred to explore most quantitative details of such effects by utilizing homogeneous self-exchange rather than solely

electrochemical processes [7,23]. This was brought about in part by the identification of a suitable series of metallocenium–metallocene reactions, of the general form $Cp_2M^{+/o}$, where Cp is a cyclopentadienyl ligand and M – Co or Fe [23]. Reliable estimates of the solvent-dependent barriers for these systems can be obtained from E_{op} values for closely related biferrocene cations [12]. This enables the solvent-dependent k_{ex} values to be corrected directly for the variations in barrier height. The substantial (up to 10^2 fold) variations in k_{ex} in a given solvent which are induced by altering Cp and/or M have been traced primarily to differences in the degree of electronic coupling (i.e., the magnitude of H_{12}) and consequently in the reaction adiabaticity [i.e., the κ_{el} value in Eq. (7)], reflecting the alterations in electronic structure and the orbital symmetry for the transferring electron.

Interestingly, the logarithmic dependence of the barrier–corrected rate constants, k_{ex}, upon r_L^{-1} in Debye–like solvents varies systematically with the magnitude of k'_{ex} in a given solvent [23a]. For the least facile redox couples (e.g., ferrocenium–ferrocene), k'_{ex} is virtually independent of r_L^{-1}, whereas for the most facile couples (e.g., $Cp'_2Co^{+/o}$, where Cp' – pentamethylcyclopentadienyl) the log k'_{ex} – log r_L^{-1} slopes approach unity at small r_L^{-1} values. This systematic behavior is consistent with a progression from virtually nonadiabatic to near–adiabatic electron transfer, reflected in the increasing emergence of solvent dynamical effects. Indeed, a detailed analysis of the solvent–dependent kinetic data yields H_{12} values for $Cp_2Co^{+/o}$ and $Cp_2Fe^{+/o}$ (ca 0.5 and 0.1 kcal. mol^{-1}, respectively) that are in accordance with independent theoretical estimates [23a].

In contrast, the corresponding solvent–dependent k_{ex} values for $Cp_2M^{+/o}$ electrochemical exchange are uniformly facile, and exhibit marked effects from solvent dynamics, apparently reflecting a greater degree of donor–acceptor orbital overlap engendered at the metal–solution interface [23b,c]. Indeed, most electrochemical reactions examined so far in this context exhibit comparable behavior. An interesting exception, however, is provided by the $Ru(hfac)_3^{o/-}$ couple (hfac – hexafluoroacetylacetonato) in that the solvent–dependent electrochemical exchange kinetics of this system are both sluggish and essentially independent of the solvent dynamics [29]. By comparison with the corresponding self–exchange kinetics and with related electrochemical systems, this behavior has been traced to the occurrence of nonadiabatic electrochemical reaction pathways [29].

Given the largely satisfactory picture noted above for metallocene self–exchange reactions in Debye–like solvents, we have been interested in exploring their behavior in "non–Debye" media (e.g., propylene carbonate, primary alcohols, water) that as noted above are characterized by additional higher–frequency solvent relaxations [25b,30]. Broadly speaking, the substantial (ca 10 fold) rate accelerations predicted from theoretical models in such media [25] are borne out by the experimental findings [25b,30]. Similar results are also obtained for some electrochemical systems [22a,31]

One issue that has received little experimental attention so far is the interplay between nuclear dynamical effects arising from reactant vibrational and overdamped solvent motion. This is probably due to the

paucity of experimental systems suitable for solvent-dependent studies for which the magnitude of the inner-shell barrier is known and (preferably) can be altered. Given the prevalence of electrochemical systems for which the inner-shell barrier is substantial, however, such studies would be of significant practical interest.

VII. CONCLUDING REMARKS

While the understanding, as well as interpretation, of electron-transfer kinetics at metal-solution interfaces has been placed on an increasingly molecular-level basis in recent years, manifold challenges remain. Even for the simplest class of reaction considered here: outer-sphere one-electron exchange processes, there are substantial uncertainties in both the activation dynamics and energetics associated with solvent reorganization. Nevertheless, the increased emphasis placed on the elucidation of preexponential factors in electrochemical kinetics, especially involving electron tunneling and solvent dynamical factors, has brought some fresh insight into this previously neglected topic. The increasing tendency to consider the properties of related electrochemical and homogeneous-phase processes in concert, rather than in isolation, is also having a beneficial effect on the level of interpretation applied to the former type of reactions.

A longstanding, yet continuing, problem concerns the reliable measurement of rate parameters for rapid reactions. The advent of "ultramicroelectrodes", with the consequent diminution of the deleterious effects of solution resistance, can contribute significantly in this regard [32], but the straightforward use of such electrodes for the evaluation of fast rate constants has apparently yet to be demonstrated.

Probably the greatest and the most significant challenges in electrochemical, as in homogeneous-phase kinetics, concern multielectron and other multistep reactions, such as coupled electron/proton and electron/atom transfers. Even though many of these reactions probably involve rate-determining single-electron steps, a major difficulty remains the estimation of the thermodynamic and structural reorganization parameters associated with electron transfer in the face of such additional steps. Nevertheless, some significant progress is being made [33], suggesting that the future of electrochemical kinetics may well include an increased breadth in the type of systems amenable to molecular-level interpretation.

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